Research Progress of Weak alkaline and Non-alkaline Compound Flooding Technology Used in the Oilfield

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***Abstract*: Research progress of weak alkaline and non-alkaline compound flooding technology was reviewed. The weak alkaline flooding system, which replaced strong alkali (NaOH) with inorganic weak alkaline (Na_2CO_3, $NaHCO_3$), buffer alkaline ($Na_2CO_3/NaHCO_3$) and organic weak alkaline (weak polymer acid sodium salt),could obtain the same recovery ratio with alkaline-surfactant-polymer flooding. The betaine combinational flooding of polymer/ampholytic surfactant and hydrophobically associating water-soluble polymer/gemini surfactant could achieve a substantial increase in recovery ratio using the synergetic effect of polymer and surfactant. The latter was more suitable for the reservoir of high temperature and high salinity. Anionic surfactant worm-like micelles flooding system, whcih had lower cost and higher recovery ratio, is expected to achieve breakthrough in the tertiary oil recovery. It is pointed that single flooding of anionic gemini surfactants with simple synthesied craft and low-cost will become future development tendency owing to its special rheological properties and surface activity replacing alkaline and polymer.**

Keywords*：weak alkaline compound flooding；polymer/surfactant compound flooding；gemini surfactant；review hydrophobically associating water-soluble polymer；

Indoor and pilot study shows that[1~3], recovery rate of alkali/surfactant/polymer (ASP) compound flooding can raised more than 20% again based on water flooding, which has good effect of oil increase and water productions decline. In the application of ASP flooding, on the one hand, strong alkali (NaOH) reacts with active component in original oil, by which it can produce natural surfactants, and generate synergistic effect with plus surfactant, greatly reduced the oil/water interfacial tension; On the other hand, it can reduce adsorption capacity of surfactant, reducing the cost of combination flooding. But the application of strong alkali brings about the complicated techniques of site construction; oil system scales; liquid producing ability of production wells declines; The cycle of pump inspection shortens; Produced liquid has difficulties in demulsification and dehydration; The viscoelasticity of polymer's solution lessens; The stratum permeability decreases due to dispersion and migration of stratigraphic clay; All these series of problems can eventually restrict the industrialization promotion and application of ASP flooding [4~6]. In addition, the successful tests of ASP flooding are carried out in comparatively nice geological conditions (such as Daqing oilfield, the temperature of oil reservoir is 45.3 and the salinity of formation water is in 4468 mg/L). However, high salinity is bound to affect the properties and compatibility of chemical agents in compound system for some oil reservoirs with high temperature and high salt. Therefore, the researches of oil flooding systems with weak alkali and even non-alkali are imperative. This paper reviews the research progress of low alkaline and non-alkaline compound flooding technology in the hope that it can induce some ideas for new oil flooding system research.

I. WEAK ALKALINE COMPOUND FLOODING TECHNOLOGY

A. ASP Compound Flooding System with the Participation of Inorganic Weak- Alkali

ASP compound flooding with the participation of inorganic weak- alkali (eg: NaHCO3) exceeds the strong alkali ASP compound flooding in terms of injection-production ability, oil production speed and emulsifying ability, etc. and moreover, it also can raise the oil recovery rate about more than 20% than that of water flooding. [7]. What's more, compared with the ordinary strong alkali ASP compound flooding, weak alkali ASP compound flooding can greatly reduce the corrosion of underground rock and the damage to oil reservoir.

The compound system made by XiaoLin Wu [8], forms the super-low interfacial tension(10-3mN/m) with crude oil within mass concentration of a wider surfactant(0.1%～0.3%) (alkylbenzene sulfonate) and alkali (Na2CO3) (0.6%～1.2%). At the same time, this system shows a strong adaptability to oil-water condition of different sections and different oil layers in Daqing Oilfield and can greatly reduce the chromatographic separation effect resulted from adsorption and remains of surfactants in geologic layers. Indoor natural core flooding experiment indicates that the average flooding efficiency of this ASP system increases by about 20% more than that of water flooding. The recovery rate of small-space-well ASP compound flooding pilot test increases by 24.66% than that of water flooding.

Research of XinJiang Yuan etc demonstrates that [9], soluble silicophosphate which substitutes for NaOH compound flooding system has the obvious effect of corrosion and scale inhibitor. It can obtain super-low water-oil interfacial tension (10-3mN/m). The profile modification effect (High, low and medium permeability core shunt) is better than that of ordinary (strong alkali) ASP compound system and polymer solution and has super capacity of water resistance and scour. The transmission capacity in porous media is as same as the capacity of the ordinary polymer solution. The extent of recovery rate is quite as same as the extent of ordinary (strong alkali) ASP compound system.

Medium and strong (pH = 9) buffer base (Na2CO3 / NaHCO3) can not only guarantee to generate petroleum soap, make full use of petroleum acid and reduce plus surfactant concentrations but also interact with stratum SiO2 and prevent the formation of silicon scale. The application of medium and strong buffer base which substitutes for strong alkali is proved to be useful in by tertiary flooding [10]. Li Yu etc., carried out research of modified natural carboxylate/buffer base/polymer flooding. It indicates that when the score of alkali quality is 1.5%(the mass ratio of Na2CO3 to NaHCO3 is 1:1) and the mass score of modified natural carboxylate, water-oil interfacial tension can achieve ultra-low. The indoor flooding effect of buffer base ASP compound flooding is 18% after polymer flooding.

In addition, studies show that [12] the application of organic alkali (weak acid sodium salt of polymer) which replaces and improves inorganic alkali used by traditional ASP compound flooding can also get super-low interfacial tension. Moreover, the organic alkali would not react with divalent cations (such as, Ca2+, Mg2+) that produces precipitation, would not affect the polymer injection liquid viscosity and can improve the polymer's properties in hard water.

B. Worm-like Micelle Weak Alkaline Flooding System

Being added salts (such as Na2CO3, Na3PO4) to ionic surfactant solution, micelle can be transformed from ball shape into stick shape and then form the wormlike micelle which can bend freely [13]. Micelles intertwine with each other and form a net-shape structure. Micelle has such characteristics as viscoelasticity, high interfacial activity, rheological controllability, and shear dilution etc., which has a wide prospect of application in terms of oil-gas recovery [14]. At present, academic researches of cation surfactants worm-like micelle are abundant[15-16].However, the application of anion surfactants worm-like micelle is limited because oil sands of formation are negatively charged and cation worm-like micelle has serious adsorption loss. The flooding system of

positive ion surfactants worm-like micelle has a bright future. Quan Cao etc. [17] get worm-like micelle made up of natural carboxylate Na_2CO_3 and the flooding efficiency is 14.1%～25.0% OOIP (Original Oil in Place) while Yongqiang Gi etc. [18] get worm-like micelle made up of natural carboxylate Na_3PO_4 and the flooding efficiency is 22.2%～32.7% OOIP. Study of Li Yu etc. [19] indicate that the indoor simulation flooding of worm-like micelle flooding formula(w/%, 1.83 NaOA+4.24 Na_2CO_3) can raise the recovery rate by 25% (OOIP). Moreover, this system can prevent the residual oil from restarting and deforming after polymer injection, gradually making the oil wall migrate toward the entrance, enlarge volume involved and increase displacement efficiency.

A. Polymer/Amphotericl Surfactant Dual Compound Flooding System

The interfacial tension of polymer/surfactant dual system, the type of whose surfactant is cation, anion and non ionic respectively, and oil has the limited capacity of reaching the lowest (10^{-3}mN/m) [20～22], which affects the flooding efficiency of dual system significantly. The interfacial tension of polymer/surfactant dual system formed by amphotericl surfactant and oil can reach the lowest and therefore it has attracted many attentions. Huifen Xia etc. [23] hold the idea that polyacrylamide/ amphotericl surfactant (carboxylic betaine) dual compound flooding system can form the lowest interfacial tension (10^{-3}mN/m). It can increase the recovery rate enormously by making use of the viscoelasticity of polymer solution and the lowest interfacial tension of surfactant system. Wenxiang Wu etc. indicate that [24] as a sacrificial agent, polymer/ sulphobetaine dual system which is non alkali and a few Na_3PO_4 added have the same flooding efficiency with the regular ASP compound system which contains strong alkali (NaOH).The added recovery value of compound flooding is more than 25% in man-made homogeneous and heterogeneous cores. The interfacial tension between this composite system and simulated fourth factory of Daqing crude oil achieve 10^{-3}mN/m orders of magnitude.

B. Hydrophobic Associating Polymer/Gemini Surfactant Oil Flooding System

At present, polymers used in the ASP flooding system are mostly partly hydrolysis polyacrylamide. Because there are a large number of cationic (such as Ca^{2+}, Mg^{2+}) in oilfield water, and inject a large sum of alkali agent from outside (bring a lot of Na^+), some hydrolysis molecular polyacrylamide cannot completely stretch, and molecular conformation results in a curly state, making viscosity decreased dramatically. Only if some hydrolysed polyacrylamides (HPAM) are put doubly, it can realize the ideal control of flow. So it can sharply increase flooding cost. The essence of hydrophobic associating polymer bring a hydrophobic group into some hydrolysis polyacrylamide molecular chain, making polymer molecules in aqueous solution, can pass between the molecules associating groups special in hydrophobic generates under the condition of electrostatic, hydrogen bonding or van der Waals force and has a certain strength but reversible physical associating, in solution of reticular formation huge three-dimensional space structure, even at relatively low molecular weight polymer and lower concentrations still have very high viscosity, rather than general partly hydrolysis polyacrylamide only by increasing the size of individual molecules in solution to realize efficient viscosify. In recent years, Gemini surfactant/hydrophobic associating polymer flooding system because of its high synergetic is good, the interfacial activities, unique rheological research and active [25]. through PuWanFen etc in simulating the zhongyuan oilfield reservoir temperature (70℃) conditions NNMB Gemini surfactant with hydrophobic associating polymer composite system and binary NAPS interfacial tension of crude oil to NNMB solution that NAPS had no significant effect on the interfacial tension value; NNMB/NAPS in binary systems, can increase sodium chloride added with a certain volume of surfactant decreasing interfacial tension efficiency; This system and crude oil the minimum transient interface between tension all low to 10^{-3}mN/m, this new type of binary system for high salinity heterogeneity of reservoir greatly enhance oil recovery

application prospect.

C. Gemini surfactants unary non-alkali flooding system

Due to its various virtues such as low critical micelle concentration CMC, high surface activity, good water solubility, anti-salt, good compatibility and unique rheological property etc., gemini surfactants shows great application potential in tertiary oil recovery [26]..

Shanfa Tang's research shows that [27], critical micelle concentration of cationic gemini surfactant two methylene group-1- double (dodecyl two methyl brominated ammonium) (C12-2-12.2 Br- 1) is only 547mg/L, and corresponding surface tension is 30.72 mN/m, which has a better surface activity compared with single-chain surfactants dodecyl sarsechim brominated ammonium (DTAB). C12-2-12.2 Br - 1 oil flooding efficiency and concentration change in coincidental relationship, with the concentration of 500 mg/L which indicates it can improve recovery ratio by 6.45%. Its effect is obviously superior to the regular DTAB single- chain surfactant, which is more suitable for improving water flooding recovery of some medium, low permeability reservoirs.

YongMing Zhang's research shows that[28], when quality score was 1%, sulfonates surfactants - petroleum sulfonates composite system can reduce water-oil interfacial tension to $4\times10^{-4}\sim6\times10^{-4}$mN・m- 1. Cooperativity between Sulfonates Gemini surfactant and petroleum sulfonates, which can enhance oil recovery.

Li Yu etc [30]quality score of synthesized Gemini surfactant carboxylic acid salts SDG - 4 was 0.005% , making water-oil interfacial tension within superlow level, and has the very good combination synergetic with the common surfactant (SDCM-1, SDC-1); The static adsorption of SDG-4 surfactants in oil-sand is 2.555 mg/g, dynamic adsorption is about 0.25 mg/g, which accords with requirements of absorption loss of chemical flooding to surfactants made by national "eight-five" and "nine-five" chemical flooding (The loss of dynamic adsorption oil sand is below 1mg/g).

To sum up, gemini surfactant contributes to the researches of ASP compound flooding with non- alkali and weak-alkali, is expected to reduce the amount of polymer, and replaces the alkali in ASP compound flooding system, which could eventually realize one flooding system and explore a new path to tertiary oil recovery of oil field.

III. CONCLUSIONS AND DEVELOPMENT TREND

1) The Weak Alkaline Flooding System made up of inorganic weak-alkali(Na_2CO_3,$NaHCO_3$),bufferbase (Na_2CO_3/$NaHCO_3$) and organic weak- alkali (weak acid sodium salt of polymer) can get the same recovery ratio as strong alkali (NaOH) ASP compound flooding could, and avoid the negative effect of strong alkali.

2) Worm-like Micelle Weak Alkaline Flooding System with anion surfactant has the advantages of lower cost and higher recovery ratio, which can be used for starting residual oil and is expected to be promoted in tertiary oil recovery.

3) The polymer/amphotericl surfactant and hydrophobic associating polymer/gemini surfactants binary systems use the synergetic between the viscoelasticity of polymer's solution and super-low interfacial tension, which can greatly increase recovery ratio. Among them, gemini surfactant/hydrophobic associating polymer system has a positive prospect in some reservoir with high salinity and heterogeneity.

4) Anion gemini surfactants with the advantages of simple synthesis craft and cheap cost has unique rheological property and high surface activity, which is expected to replace alkali and polymer to realize one flooding.

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